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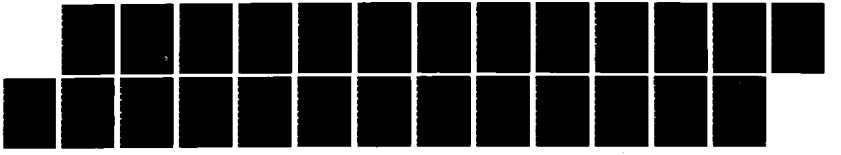

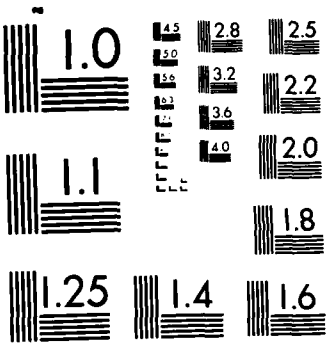

October, 1985

PRODUCTION OF FINE POWDERS FOR PERMANENT MAGNETS USING A D.C. ARC PLASMA

by

Huk Y. Cheh and Thomas J. Dougherty
Chemical Engineering Laboratories
Department of Chemical Engineering and Applied Chemistry
Columbia University in the City of New York
New York, New York 10027

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Scientific program Officer

Director, Metallurgy & Ceramics Program
Materials Science Division
Office of Naval Research
800 North Quincy Street
Arlington, Virginia 22217

Prepared for

OFFICE OF NAVAL RESEARCH
DEPARTMENT OF THE NAVY
800 NORTH QUINCY STREET
ARLINGTON, VIRGINIA 22217

ABSTRACT

Powdered feeds of iron (-100 mesh and -325 mesh) Crumac (Mn3AlC, various sieved fractions) entrained in argon were fed into a D.C. arc through a Forced Convection Cathode. The arc effluent was quenched with argon and the products collected in a cyclone and Pulsaire baghouse. The samples were collected and stored under argon. All samples were obtained in runs where the oxygen concentration was less than 0.02%. All products oxidize on contact with air. The baghouse products from the iron runs are frequently pyrophoric, igniting in air. The object was to prepare rapidly quenched, submicron powders of high coercive force for use in permanent magnets.

The electrical conductivity of the feed and products proved to be the major source of difficulty in this work. The products and unvaporized feed would collect on the arc chamber walls and never reach the cyclone and baghouse. This problem was partially solved by applying a negative potential (-100 v) to the chamber. Useful product was obtained in only five runs (three with iron, two with Crumac), near the end of this project. The products from the three iron runs were combined into two samples, one cyclone product and one baghouse product. These two samples, along with the baghouse products from the two Crumac runs were shipped to Crucible Research Division of Colt Industries.

The highest surface areas of the baghouse products were 27 m^2/g for iron and 42 m^2/g for Crumac. The surface area was measured on samples that had been exposed to air and undoubtedly oxidized. All samples appeared to be heterogeneous, at least after exposure to air.

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INTRODUCTION

The purpose of this investigation was to prepare rapidly quenched, submicron samples of metals and alloys for evaluation as materials for permanent magnets. The samples were to be prepared by vaporization of a suitably selected feed material in a D.C. electric arc followed by rapid quenching. The objective was to obtain materials with high coercive force. Only two materials were actually employed in this work, iron and an alloy known as Crumac (Mn3AlC). The perovskite structure of Crumac is ferromagnetic. Furthermore, alloys of Mn and Al have been found to exist in unusual structures composed of space-filling but non-periodic units. It has been suggested that materials of this type might have interesting magnetic properties. Although there was not much doubt that submicron metals and alloys could be produced by condensation form the vapor generated by the arc, the extent of the practical difficulties in accomplishing this effectively was not foreseen.

In general, we would not expect particles condensed from vaporized alloys to be homogeneous in composition. For alloys of elements of very different vaporization temperatures, we would expect considerable segregation unless the elements form stable compounds in the vapor phase, as with some carbides and nitrides. One might well expect that mixtures of different powders would serve as well as alloys as feeds. Whether the formation of heterogeneous products would be beneficial or deleterious in any given system or application is an open question. In short, this work was of necessity of a general exploratory nature.

The bulk of this report deals with the technique required to prepare the samples. The only property of the samples produced that was measured was surface area. Samples were examined under a (light) microscope to see if there was any obvious heterogeneity. The response of the products to a weak magnet was also noted. As will be seen in what follows, the major experimental problems resulted from the electrical conductivity of the feed material, although the high density and magnetic properties might also have played a role.

This work was performed in two phases. The original contract contract was for a four month period scheduled to begin September 1, 1981. Delays in processing made it necessary to postpone the starting date to October 1, 1981. Experimental work was halted on February 12, 1982. A two month extension was requested and granted and work resumed in mid-October of 1982 and terminated December 20, 1982. It was only in November and December of 1982 that samples in any significant quantity were produced.

EQUIPMENT

A sketch of the overall system is shown in Figure 1. It consisted of a D.C. arc unit followed by a cyclone, baghouse and blower. Peripheral equipment included a powder feeder, splitter, oxygen meter (on-line), Quantasorb surface area meter, screens for sieving, rotameters for metering gas flows, etc.. The principal components of the arc unit were: three D.C. power supplies; a small welding generator; high voltage R.F. striker; a Fluid Convection Cathode (FCC); three Fluid Transpiration Anodes; and a quench chamber with four quench jets. A sketch of the FCC is shown in Figure 2 and an FTA in Figure 3. The jets were simply four 1/2" stainless steel tubes crimped at the end to yield a roughly rectangular orifice about 0.050" high by 0.50" wide. These jets were roughly 2.5" below the center line of the anodes and bent downwards at an approximately 30 degree angle to minimize turbulence. Thus the gas jets intersected the tail flame of the arc about 3.5" below the center line of the anodes. It would have been preferable to hit the tail flame at least one inch higher, but this was not possible with the existing equipment. The jets were positioned as close as possible to the tail flame or about 2" off the arc axis. Although these quench jets may appear primitive, they are effective and superior to several others that we have tried.

The arc was ignited by striking a pilot arc to a carbon anode which then ignited the three FTA's. An R.F generator created a spark between the cathode and carbon anode and a small D.C. welding generator (motor-generator) supplied the current for the pilot arc. Three larger (rated at 250 Amperes each) D.C. power supplies (silicon rectifiers) supplied the current to the three FTA's. The current to each anode was individually controlled. After the arc was lit, the small welding generator was turned off, the switch to the carbon anode opened, the carbon anode withdrawn, and the striker port (which doubles as a viewport) sealed. The plugs in the view ports contained quartz windows and lenses focused the exiting radiation onto translucent screens to provide images of the arc.

The powders were fed from a small TAFA powder feeder with argon as a carrier gas. The gas-solid stream passed through a four-way splitter and

thence to the four feed lines in the cathode body. The thoriated tungsten tip was protected by a stream of argon which passed through an annular inner shroud. Argon through the porous graphite plugs of the FTA's made electrical contact with the central column of the arc. The quench gas was argon. All gas flows were measured with rotameters.

The cathode was grounded and the arc chamber electrically floating. Voltage breaks (more accurately, current breaks) of Teflon isolated the cathode and anodes from the chamber. Teflon inserts in the flange ahead of the cyclone isolated the chamber from the cyclone and baghouse, which were grounded. A small D.C. power supply (0.5 amp) was used to charge the chamber to a negative voltage (usually 100v) to prevent the negatively charged particles from striking the walls, discharging, and collecting thereon. The chamber would otherwise have been at a positive potential, approximately that of the anodes, because of current leakage from the anodes.

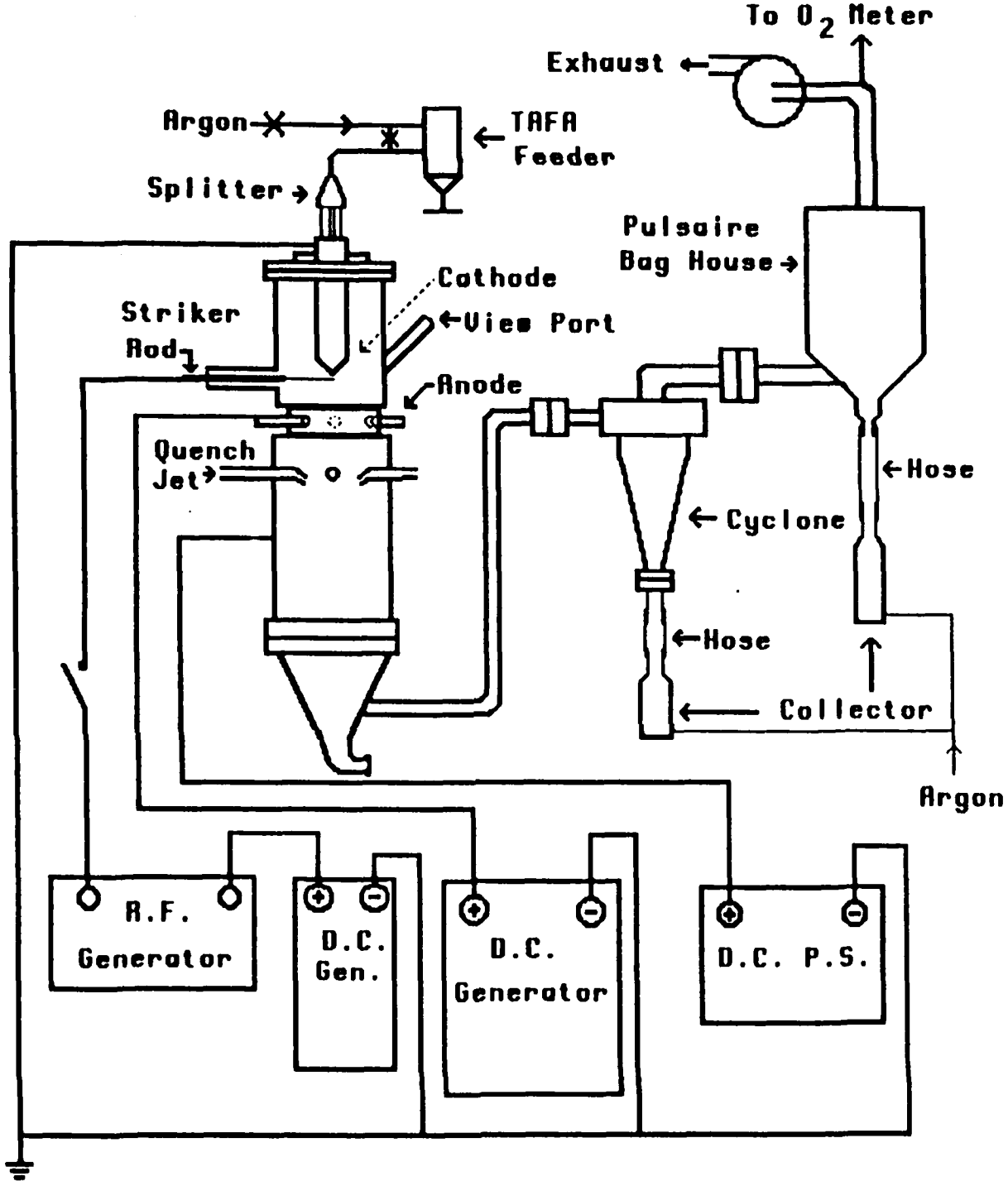

Figure 1. Sketch of Arc Unit.

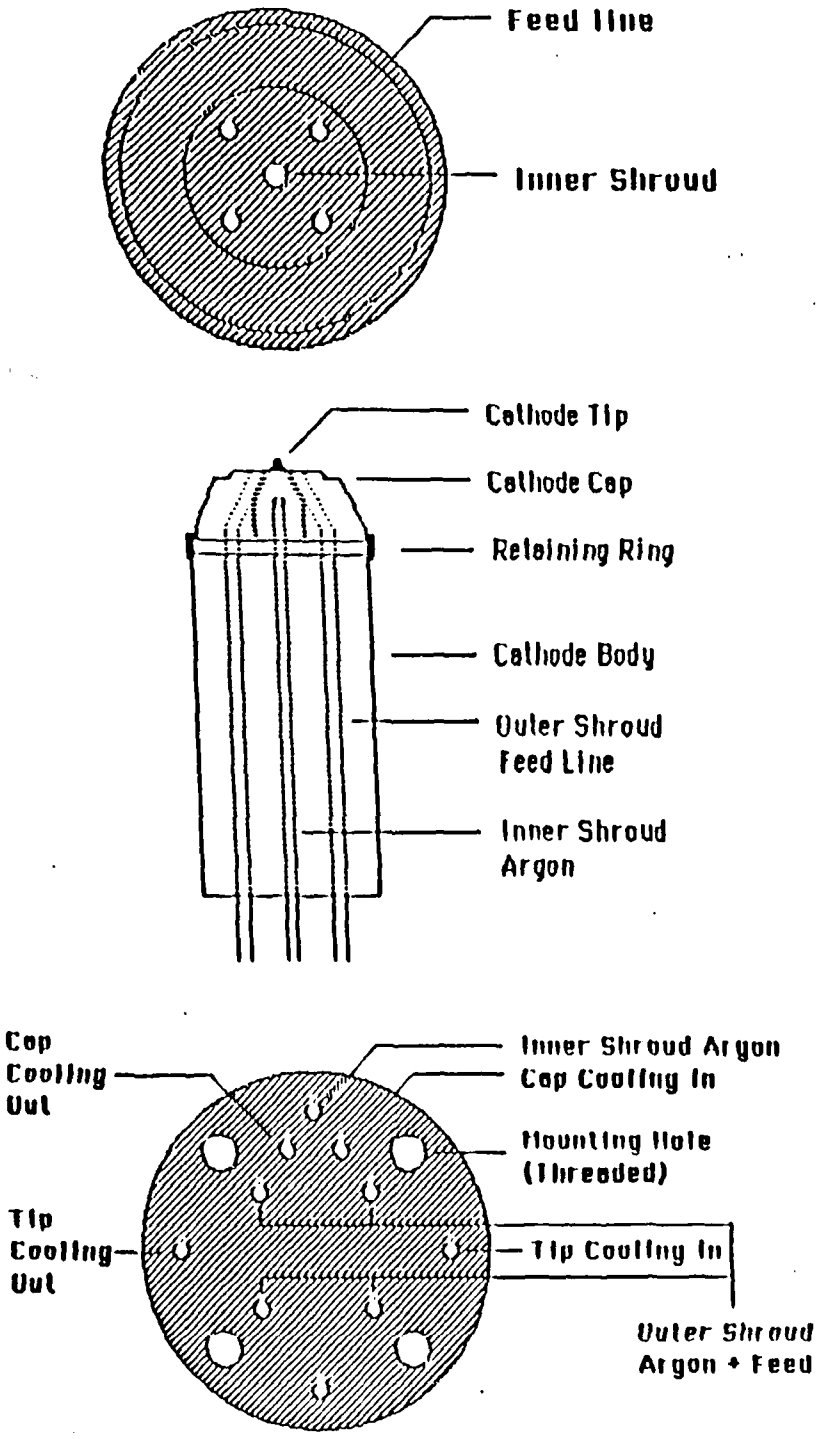

FIGURE 2. SKETCH OF FORCED CONVECTION CATHODE.

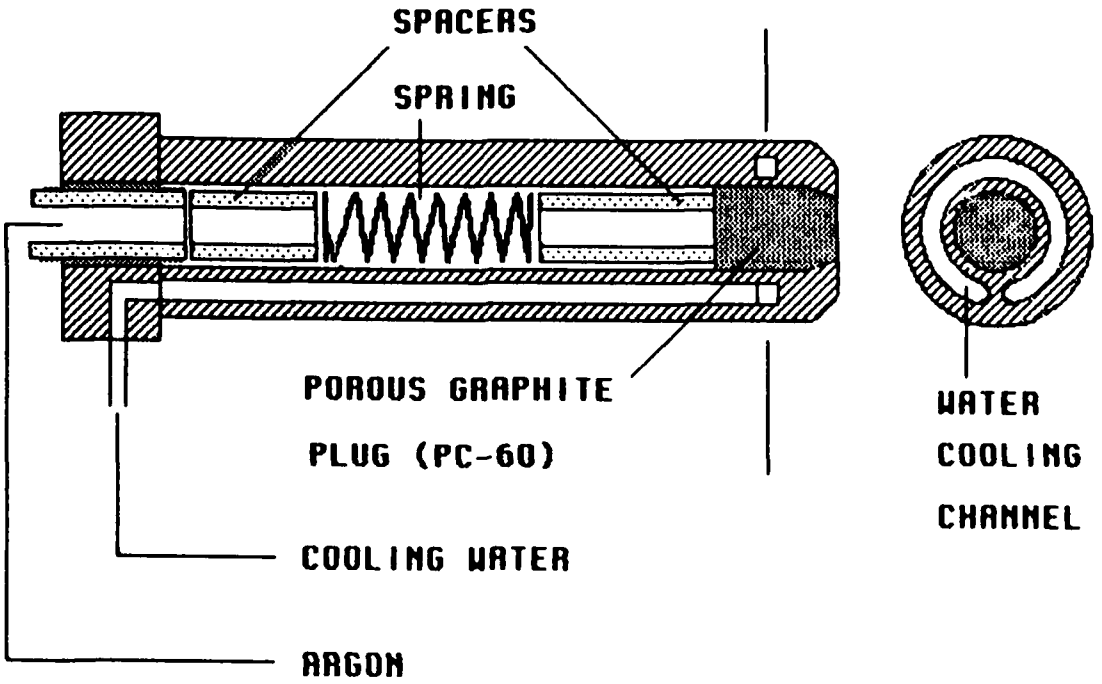

FIGURE 3. SKETCH OF FLUID TRANSPIRATION ANODE.

EXPERIMENTAL METHODS AND RESULTS

Since the principal result of this work was the development of techniques to produce the submicron particles, procedures and results have been combined in this section. In the first phase of this work, there were nine runs in November, seven in December and another seven in January of 1982. The last test was performed on February 12, 1982. The duration of these runs ranged from 12 to 60 minutes which represented the time that powder was fed to the arc. The longer the length of the run, the more likely it was to end disasterously. The oxygen content of the exit stream ranged from 0.01 to 0.08%, with 0.04% being typical. All of the tests were performed using iron powder as feed. At first -100 mesh iron powder was used but this did not appear to vaporize significantly and in November the feed was changed to -325 mesh iron powder.

These early tests were plagued with arc instabilities, poor powder feeding, and plugging of feed and exit lines. Considerable damage was done to various parts of the cathode assembly when the arc jumped from the tungsten tip. The tips would then be covered with iron and could not be reused. Numerous retaining rings, caps, and shrouds were destroyed. In one instance, the retaining ring was fused to the cathode body and was removed only with great difficulty and some damage to the cathode body. Iron would fuse in the feed slots and often could not be removed. The feed tubes in the cathode body would plug. Sometimes these plugs could be removed by physical means but, more often, the feed tubes had to removed and the iron dissolved by acid, or the tubes replaced.

Perhaps the most significant, although not the most destructive, problem was the accumulation of material in the quench chamber and around the anodes. Practically no product was obtained in the cyclone and baghouse. This material would blanket the walls of the chamber and then slough off and fall into the exit pipe, eventually sealing this pipe completely. This material had to be removed from the pipe by driving a steel rod through the blockage and, in some cases, drilling through. In addition, because of the electrical conductivity of the metal, the chamber would short to the anodes and to ground. On two occasions, arcs jumped the voltage breaks and burned holes in the cyclone.

At first, since we were trying to obtain useful products, the system was thoroughly cleaned after each run. The results of three of these runs are shown in Table 1 for comparison with later results. This disassembly and cleaning was a laborious and time consuming process. It was clear that unless the operation could be substantially improved, no significant quantity of product could be produced. Attention was, therefore, focused on improving operation. The problems to be resolved were:

1. Improve arc stability
2. Improve powder feeding
3. Improve electrical isolation of anodes and chamber
4. Find a method to prevent accumulation of material in the quench chamber

Rather than describe the different attempts made to resolve these problems, we will simply discuss the methods that finally proved to work reasonably well.

Plugging of the exit pipe was eliminated by moving the take-off point from the bottom of the conical section to the side of the cone. This change was made in late January and early February of 1982, partly out of desperation, but principally because the last run in January resulted in a hole inside the quench chamber allowing water to leak from the water channel into the chamber. This required cutting through the water channel, welding the hole, and resealing the water channel. During this time, since the unit had to be completely dismantled, we took the opportunity to make several changes, one of which was moving the exit pipe. In addition, all voltage breaks were replaced with larger and better designed pieces of Teflon. For example, the voltage break at the flange ahead of the cyclone was given a sleeve that reached four inches back into the pipe. The supporting plate at the base of the quench chamber was replaced and insulated from the frame with all new and heavier pieces of transite. We hoped to have optimum conditions for one last attempt but, unfortunately, we neglected to check the filter bags.

The last run at first appeared disappointing since no pressure drop was observed across the baghouse. However, a reasonable amount of material appeared in the cyclone and on the cyclone wall and the pipes and baghouse walls were coated with product. Examination of the filter bags revealed the presence pf several large holes. Since the oxygen

concentration was low (<0.02%) throughout this run, it must be concluded that in the preceding run sufficient material reached the baghouse to burn holes in the bags when exposed to air. Furthermore, the sample filter was filled with black powder. This result was sufficiently encouraging to induce us to ask for a two month extension.

The inital runs in the second phase were not very encouraging. The buildup on the chamber walls returned. It finally occurred to us that electrical effects were causing the chamber to act as an electrostatic precipator and that our one encouraging test was probably due to the fact that the insulators were all new and exceptionally clean. In order to prevent or retard the accumulation of material on the chamber walls, a small D.C. power supply was installed to charge the walls to a negative potential and thus, hopefully repel the negatively charged particles. The first power supply had only a 12 volt output and proved completely inadequate and was immediately abandoned. A high voltage (up to 6 kvolt) power supply was installed but this power supply was rated for only 25 mA. Nevertheless, this unit functioned throughout the run (11/16/82, Table 2) but the current could not be measured since the ammeter scale only reached 25 mA and the pointer remained pinned at the end of its range (estimated at 30 mA) throughout the time of powder feeding. A third power supply was borrowed and installed for the run of 11/19/82 (Table 3). This unit had rated output of 500 ma and voltage to 500 volts. After 60 minutes the 0.5 A fuse blew and was replaced by a 1 A fuse which blew at the 90 minute mark and was replaced by a 2 A fuse. Shortly after, the power supply started to smoke and arc and was turned off for the remainder of the run. This power supply was used in the remaining tests and functioned reasonably satisfactorily (Tables 4, 5, and 6). An unanticipated, but welcome, bonus of the negative charge on the walls was an improvement in arc stability. It appears that the elecric field holds the arc more firmly on its axis.

The electrical isolation of the anodes was continually being improved by changing the type and size of the insulating sleeves. After trying several materials (transite, lava, boron nitride), Teflon was found to be most suitable. The Teflon was shielded from the heat of the arc by a layer of Cotronics (alumina) which eventually was installed to completely cover the inside wall of the chamber in the vicinity of the anodes.

TABLE 1. SUMMARY OF YIELD AND SURFACE AREA OF PRODUCTS

RUN DATE	FEED TYPE	FEED MESH(1)	FEED GM	FEED MIN	FEED GM/MIN	PRODUCT CYCLONE GM	PRODUCT CYCLONE M^2/GM	PRODUCT BAGHOUSE GM	PRODUCT BAGHOUSE M^2/GM
11/05/81	Fe	-100	355	45	7.88	7	2.1	6	18
11/09/81	Fe	-100	550	60	9.17	10	4.5	13	23
11/10/81	Fe	-100	510	60	8.50	15	3.8	8	15
11/16/82	Fe	-325	710	80	8.88	31	4.5	25	27
11/19/82	Fe	-325	1373	120	11.44	18	5.8	56	8(2)
								100	26
12/07/82	Fe	-325	700	60	11.67	106	16.1	55	26
								70	7
12/10/82	Crumac	-140 +170	650	46	14.13	139	3.1	17	24
								70	31
12/14/82	Crumac	-100 +140	996	60	16.60	290	3.2	283	42
12/20/82	Crumac	-270 +325	404	31	13.03	--	--	26	11(3)

(1) Surface area of Fe-325 = 1.04 m^2/g.
Surface area of Crumac-270+325 = 0.16 m^2/g.

(2) Sample rust-red color.

(3) Sample oxidized. White snowball-like agglomerates visible under microscope.

TABLE 2. OPERATING CONDITIONS FOR RUN OF 11/16/1982

FEED: IRON POWDER (-325 MESH)
FEED RATE: 710 GM/80 MIN = 8.88 GM/MIN
ARC GAP: 6.1 CM
VOLTAGE: 70-80 VOLTS
CURRENT: 330 A (110 A each anode)

GAS FLOWS (L/MIN ARGON)		PRODUCT	GMS	M^2/GM
INNER SHROUD	5.7	BAGHOUSE (PULSED)	25	27
OUTER SHROUD	16.8	BAGHOUSE (BRUSHED)	---	--
THREE ANODES	18.0			
FOUR QUENCH JETS	568	CYCLONE	31	4.5

TIME MIN.	CHAMBER PRESSURE PSIG	ΔP, BAGS PSIG	D.C. POWER SUPPLY(1) VOLTS	MAMP
	ARC OFF - FEED OFF		100	4
	ARC ON - FEED OFF		100	25
0	FEED ON 0.8	0.02	0-100	25
10	0.8	0.1	0-100	>30
20	0.9	0.2	0-100	>30
40	1.0	0.3	0-100	>30
60	1.2	0.5	0-100	>30
80	FEED OFF - ARC OFF		100	10

(1) High Voltage D.C Power Supply. Rated D.C. Output = 25 ma. Ammeter scale reads only to 25 ma and pointer was off scale most of the run.

TABLE 3. OPERATING CONDITIONS FOR RUN OF 11/19/1982

FEED: IRON POWDER (-325 MESH)
FEED RATE: 1373 GM/120 MIN = 11.44 GM/MIN
ARC GAP: 5.1 CM
VOLTAGE: 70-80 VOLTS
CURRENT: 330 A (110 A each anode)

GAS FLOWS (L/MIN ARGON)		PRODUCT	GMS	M^2/GM
INNER SHROUD	5.7	BAGHOUSE (PULSED)	56	8
OUTER SHROUD	20.0	BAGHOUSE (BRUSHED)	100	26
THREE ANODES	18.7			
FOUR QUENCH JETS	620	CYCLONE	18	5.8

TIME MIN.	CHAMBER PRESSURE PSIG	ΔP, BAGS PSIG	D.C. POWER SUPPLY(1) VOLTS	MAMP
	ARC OFF - FEED OFF		100	4
	ARC ON - FEED OFF		100	25
0	FEED ON 0.8	0.02	0-100	25
20	0.8	0.1	0-100	100-200
40	0.9	0.2	0-100	100-300
60	1.0	0.3	0-100	>500(2)
90	1.2	0.5	0-100	>1000(3)
120	FEED OFF - ARC OFF		----	---

(1) D.C Power Supply. Rated D.C. Output = 500 ma. Ammeter reads only to 500 ma.
(2) Fuse blown. Changed 0.5 A fuse to 1 A fuse.
(3) Fuse blown. Changed 1A fuse to 2A fuse. Power supply starting to smoke - turned off for remainder of run.

TABLE 4. OPERATING CONDITIONS FOR RUN OF 12/07/1982

FEED: IRON POWDER (-325 MESH)
FEED RATE: 700 GM/60 MIN = 11.67 GM/MIN
ARC GAP: 6.1 CM
VOLTAGE: 75-85 VOLTS
CURRENT: 330 A (110 A each anode)

GAS FLOWS (L/MIN ARGON)		PRODUCT	GMS	M^2/GM
INNER SHROUD	5.7	BAGHOUSE (PULSED)	55	26
OUTER SHROUD	20.0	BAGHOUSE (BRUSHED)	70	7
THREE ANODES	18.7			
FOUR QUENCH JETS	603	CYCLONE	106	16.1

TIME MIN.	CHAMBER PRESSURE PSIG	ΔP, BAGS PSIG	D.C. POWER SUPPLY(1) VOLTS	MAMP
	ARC OFF - FEED OFF		100	4
	ARC ON - FEED OFF		100	25
0	FEED ON 0.8	0.02	100	25
10	0.8	0.1	0-100	50-100
20	1.0	0.3	0-100	100-200
35	1.1	0.4	0-100	150-300
50	1.3	0.5	0-100	200-500
60	FEED OFF - ARC OFF		100	10

(1) D.C Power Supply. Rated D.C. Output = 500 ma. Ammeter reads only to 500 ma.

TABLE 5. OPERATING CONDITIONS FOR RUN OF 12/10/1982

FEED: CRUMAC POWDER (-140+170 MESH)
FEED RATE: 650 GM/46 MIN = 14.13 GM/MIN
ARC GAP: 5.1 CM
VOLTAGE: 55-60 VOLTS
CURRENT: 300 A (100 A each anode)

GAS FLOWS (L/MIN ARGON)		PRODUCT	GMS	M^2/GM
INNER SHROUD	5.7	BAGHOUSE (PULSED)	17	24
OUTER SHROUD	14.8	BAGHOUSE (BRUSHED)	70	31
THREE ANODES	17.0			
FOUR QUENCH JETS	561	CYCLONE	139	3.1

TIME MIN.	CHAMBER PRESSURE PSIG		ΔP, BAGS PSIG	D.C. POWER SUPPLY VOLTS	MAMP
	ARC OFF - FEED OFF			100	4
	ARC ON - FEED OFF			100	25
0	FEED ON	1.0	0.02	100	25
3		1.0	0.3	100	20-80
18		1.1	0.4	50-100	40-100
28		1.2	0.5	0-100	60-140
33		1.3	0.6	0-100	100-200
38		1.4	0.7	0-100	100-200
43		1.5	0.75	0-100	120-250
46	FEED OFF - ARC OFF			100	15

TABLE 6. OPERATING CONDITIONS FOR RUN OF 12/14/1982

FEED: CRUMAC POWDER (-100+140 MESH)
FEED RATE: 996 GM/60 MIN = 16.60 GM/MIN
ARC GAP: 6.1 CM
VOLTAGE: 75-85 VOLTS
CURRENT: 330 A (110 A each anode)

GAS FLOWS (L/MIN ARGON)		PRODUCT	GMS	M^2/GM
INNER SHROUD	5.7	BAGHOUSE (PULSED)	283	42
OUTER SHROUD	18.8	BAGHOUSE (BRUSHED)	---	--
THREE ANODES	18.7			
FOUR QUENCH JETS	568	CYCLONE	290	3.2

TIME MIN.	CHAMBER PRESSURE PSIG	ΔP, BAGS PSIG	D.C. POWER SUPPLY VOLTS	MAMP
	ARC OFF - FEED OFF		100	4
	ARC ON - FEED OFF		100	25
0	FEED ON 0.8	0.02	100	25
15	0.8	0.15	0-100	30-50
30	1.0	0.4	0-100	40-60
40	1.2	0.6	0-100	40-60
50	1.3	0.7	0-100	40-60
55	1.5	0.8	0-100	40-60
60	FEED OFF - ARC OFF		100	10

Powder feeding was greatly improved by several modifications. At first we tried a small TAFA feeder but this feeder had never worked very well, and this time proved no exception. Eventually the feed control screw became jammed and the handle snapped as a result of excessive force applied while attempting to shut off the feed. A small powder feeder was constructed from 3" pipe with a Teflon cone threaded into it. The feed was controlled by a tapered Teflon plug attached to a threaded rod to provide a variable annular orifice. The ouput of this feeder was fed to an ejector. Various modifications were made to this device which functioned, but not very well. Upon dismantling the TAFA feeder, it was discovered that an O-ring seal was missing which allowed powder to get into the threads on the feed control shaft. The O-ring was replaced and a layer of silicone vacuum grease was applied to the shaft between the two O-rings and the handle was repaired. This resolved many of the problems with the feeder but smooth powder feeding was still not achieved. The difficulties appeared principally when turning the feed on and off. A bypass was installed which allowed us to gradually introduce the carrier gas into the feeder while maintaining full gas flow through the cathode. Finally, the splitter was removed from the top of the cathode and four six-foot lengths of translucent tubing were used to connect the four output lines of the splitter to the cathode feed lines. The ID of all lines was matched to provide a smooth path from the splitter to the cathode. This modification provided a longer path to allow disturbances produced by the splitter to damp out. The translucent nature of the plastic tubing also made it possible to observe any plugging of the feed lines.

The contract was rapidly drawing to a close but we were finally able to obtain reasonable operation. Only five worthwhile runs could be made. In all of these test the oxygen concentration was maintained below 0.02%. A sixth attempt (12/20/82) ended when the arc jumped and burned a hole in the cathode cap. Unfortunately, this run had to be performed by our technician working alone since the principal investigator (TJD) was called to Jury duty and could not be excused. It had been hoped that this last test would prove to be the best since we had reserved our finest fraction of Crumac powder (-270 mesh) for the final run. In fact, our best results were achieved with the coarsest Crumac fraction (-100+140 mesh, 12/14/82). In view of the limited amount of data and the continual modification in the apparatus, this fact may or may not be significant. The

most striking result was the much smaller current (40 to 60 mA) in the 12/14/82 run, probably due to inproved electrical isolation of the chamber.

Ironically (no pun intended), the Crumac runs proceeded much more smoothly than those with iron powder feed. Operation was better and yields were higher with Crumac feed. However, since not all of the material vaporized reaches the baghouse, the actual amount of product produced is not exactly known. Particularly noteworthy is the high surface area (16.1 m^2/g) of the 106 grams of cyclone product obtained in the final iron run (12/07/82). Furthermore, the amount of high surface area material held up in the chamber can be significant. The iron powder was used because we had very little Crumac feed with which to work, especially after sieving to obtain well-defined fractions. We did not want to use this material while we were attempting to "iron out" operational problems.

DISCUSSION OF RESULTS

The only really significant result of this work was to show that it is possible to produce a product with a reasonably high surface area (around 25 m^2/g for iron and 40 m^2/g for Crumac). Undoubtedly, with more effort and better quenching, these values can be raised substantially. The yields achieved were not very high although a 28% yield of 42 m^2/g product in the Crumac run of 12/14/82 (Table 6) is very respectable for an argon arc of this size. Suprisingly, this result was obtained with the coarsest feed and highest feed rate. The fact that the highest surface area was obtained under conditions of maximum concentration of vaporized material in the gas phase was certainly unexpected.

The measured values of the surface areas are probably of only qualitative significance and are, very likely, lower bounds to the true values. This is particularly true of the values measured for the baghouse products from the iron runs. The samples taken for surface area measurement were exposed to air and were undoubtedly oxidized. The iron sample from the run of 11/19/82 (Table 3), with a measured surface area of 8 m^2/g, was a rust-red color.

All products are magnetizable and respond to a small magnet. The smaller the particle size, the more difficult the sample is to magnetize; i.e., the material from the chamber responds more readily than the cyclone product which, in turn, responds more readily than the baghouse product. Whether this is a result of the smaller particle size or a higher degree of oxidization of the smaller particles is not known.

All samples are undoubtedly heterogeneous, at least after exposure to air. Absorption of nitrogen from helium (during the surface area measurement) shows two peaks on cooling to liquid nitrogen temperature. Only a single peak is observed on desorption, which is not surprising since the temperature rise from liquid nitrogen temperature is, initially, very rapid during heating. This phenomena has occasionally been observed with other materials (e.g. fumed silica) and probably is indicative of at least two types of surface sites. The surface area of the Crumac sample from 12/20/82 was only 11 m^2/g and examination of this material under a light

microscope revealed the presence of white agglomerates (snowballs) interspersed with black and brown particles. Whether this segregation resulted from oxidation or whether the material precipitated from the vapor as a heterogeneous mixture is not certain but segregation during condensation seems to be the most plausible conclusion.

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